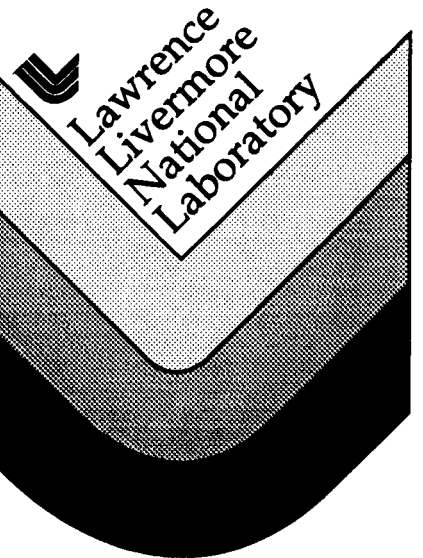


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Conduction Band States and the 5d-4f Laser Transition of Rare Earth Ion Dopants

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Abstract

We discuss how the interactions of the 5d orbital with the conduction band of the host medium play a crucial role in determining whether rare earth containing materials can serve as **useful** laser materials, based on their 5d - 4f transition. To explore this issue, we examine the pump-probe spectra of **Sm²⁺**, **Eu²⁺**, and **Ce³⁺** dopants in various fluoride and chloride crystals. In addition we suggest that the luminescence properties are also profoundly impacted by this interaction. The outstanding **UV** laser **performance** achieved by the **Ce:LiSrAlF₆** crystal is rationalized in terms of the reduced overlap of conduction band states with the **cerium** ions.

1. Introduction

The viability of laser materials is impacted by a multitude of issues, ranging **from** **fundamental** physics, to thermal issues, fabrication costs, crystal growth, and many other factors. In this paper, the **full** scope of these factors can hardly be addressed in detail. However, there is one aspect of the fundamental physics of laser materials that warrants special attention, and forms the subject of this article -- the impact of the conduction band (**CB**) states on the 5d orbital of rare earth (**RE**) ions. This aspect of the solid state physics of **RE-doped** insulators has gradually been unraveled over the last two decades. First, it has become understood that an intense **transition**, arising from the transfer of a 5d electron to the conduction band of the host can potentially interfere with the possibility of gain from the 5d-4f transition. This was recognized to be the problem for the cases of **Eu²⁺**:CaF₂ and **Ce³⁺**:Y₃Al₅O₁₂.¹ An improved understanding of these interactions by way of photo-ionization studies was also achieved, by exploring the spectral dependence of the photoconductivity. These experimental campaigns amounted to direct observations of the 4f - CB transitions, and accordingly the energetic depth of the **RE** level from the bottom of the CB.² In Fig. 1, we schematically illustrate that chief mechanisms by which the **RE** ion can be impacted by the CB states, including the presence of radiative (excited state) transitions **from** the 5d orbital to the CB, and of transitions whereby the **CB** provides a pathway to deactivate the excited state **nonradiatively** to the ground state. Another crucial aspect of these material systems is the tendency for the electron to be liberated from the **RE** and become trapped at a defect, forming a color center.³

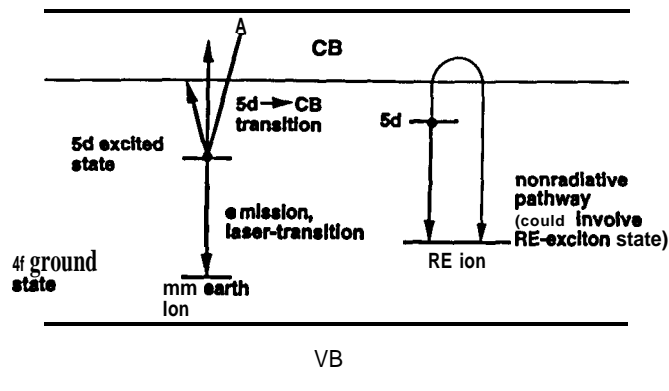


Figure 1: Illustration of how the conduction band of the host medium interacts with the 5d orbital of the rare earth ion, giving rise to both radiative and nonradiative effects.

The main objective of this article is to suggest that we as a community have now collected enough **information** to reasonably conclude that the 5d - CB interactions are a key issue that needs to be considered when trying to understand or devise a laser material that functions based on the 5d - 4f electronic transition. We have published a series of detailed papers on the various aspects of this phenomenon, and cannot include in the current context all the experimental evidence and numerical deductions. Instead we have focused here on describing the essential features of this **concept**, and recommend that the interested reader refer back to the original publications to retrieve the accounting of how the experiments were conducted, the precise values of the cross sections, and other such detailed information.

2. Sm^{2+} -doped Crystals and Glasses

Although $\text{Sm}^{2+}:\text{CaF}_2$ was one of the first laser materials to be **demonstrated**,⁴ and the laser action is based on the 5d-4f electronic transition, no **further** lasers of this nature were subsequently reported. (Recall that subsequent reports of laser action for $\text{Sm}^{2+}:\text{SrF}_2$ and other samarium-based materials were based of the 4f-4f transitions.) As it turns out, the challenges facing the Sm^{2+} ion **lasing** on the 5d - 4f transition are substantial, both in terms of nonradiative decay issues as well as excited state absorption.

The pump-probe spectroscopy displayed in Fig. 2 below speak to the fortuitous manner in which laser operation of $\text{Sm}^{2+}:\text{CaF}_2$ was **achieved**.⁵ The negative feature appearing between 700-800 nm corresponds to the well-known emission of $\text{Sm}^{2+}:\text{CaF}_2$, and the other negative-going band centered at 620 nm is the bleaching of the ground state absorption of this crystal. What is truly **fascinating** is the observation of the enormously strong excited state absorption (ESA) at 500 nm, corresponding to the 5d - CB transition. In the case of $\text{Sm}^{2+}:\text{CaF}_2$, the weak gain feature *happens* to occur in a wavelength region where the ESA has tapered off to a very low level. Also note the additional weak 5d - 4f ESA band that resides at wavelengths longer than the gain region.

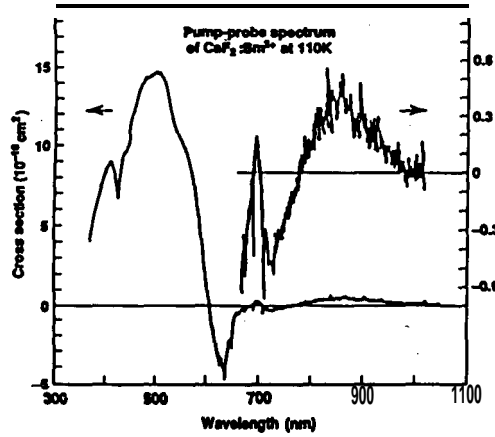


Figure 2: Pump-probe spectrum of $\text{Sm}^{2+}:\text{CaF}_2$, showing the 5d - 4f gain region at 730 nm, the 5d - 4f ESA at 800 nm, and the 5d - CB transition at 500 nm.

The emission lifetimes of Sm^{2+} in the fluorite-structure crystals are plotted as a **function** of temperature in Figure 3.⁶ The full curves are the calculations including the effects of nonradiative and radiative decay, and the dashed curves are the hypothetical curves where the nonradiative component is omitted. It is readily apparent that the trend is as BaF_2 - SrF_2 - CaF_2 - SrCl_2 , in order of the decreasing influence of nonradiative decay. The actual fitted values of the activation energies is 0.03, 0.15, 0.28, and >0.8 eV. An interpretation of these activation energies is that it is strongly correlated with the depth of the 5d level below the edge of the CB in these crystals. The calculation of the depth from the electrostatic theory of Pedrini, et al.² yields 0.1, 1.2, 1.9, and 3.8 eV. The trend is in the same rank order, and the **factor** of ~ 5 is accounted for on the basis of the expected difference between optical and thermal energies. This **information** is taken to suggest that the CB somehow opens up a route by which nonradiative decay can take place. One of the ideas discussed concerning the mechanism of this pathway entail the formation of an **intermediate** exciton-RE complex.⁷

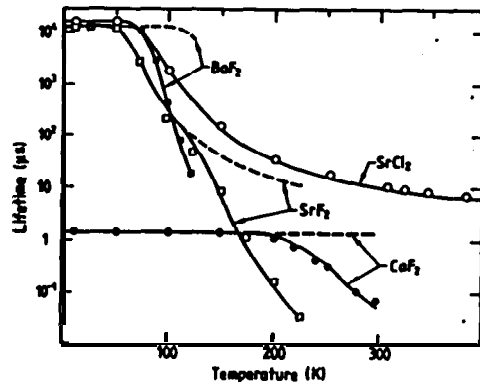


Figure 3: Emission lifetimes of Sm^{2+} -doped fluorite-structure crystals.

3. Eu^{2+} -doped Crystals

A related series of experiments were conducted on a variety of Eu^{2+} -doped crystals. The main differences compared to the Sm^{2+} systems are that Eu^{2+} containing crystals tend to **luminesce** efficiently at room temperature, and that divalent europium has not been previously reported to **lase** in any crystals or glasses. The reason for the absence of **lasing** can be easily deduced from the data shown in Fig. 4, where it is seen that the ESA overlaps the **blue/UV** luminescence in every case. The other compelling information that can be gleaned from Fig. 4 is that the ESA again follows the trend observed earlier of $\text{SrF}_2\text{-CaF}_2\text{-SrCl}_2$. Interestingly it is seen that the LiCaAlF_6 host offers the remarkable property of shifting the 5d - CB ESA further into the **UV** than any of the other materials.

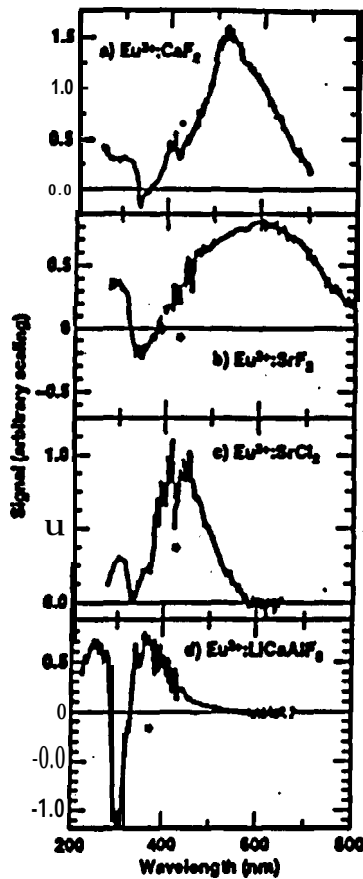


Figure 4: Pump-probe spectra of several Eu^{2+} -doped crystals, showing how the 5d - CB transition is sensitive to the separation of the 5d state from the conduction band of the host.

The data collected from the **divalent** samarium and europium-doped crystals strongly suggests that the interaction of the 5d orbital with the **CB** is a critical factor impacting the luminescence efficiency and the ESA band, and accordingly whether the material can potentially serve as a viable laser material.

4. Ce^{3+} -doped LiSrAlF_6 and LiCaAlF_6

Ce^{3+} -lasers are also based on the 5d - 4f transition, and researchers have demonstrated laser action from several laser materials in the past. But until the introduction of $\text{Ce}:\text{LiCaAlF}_6$ by Dubinskii and coworkers,⁸ the reported efficiencies were very low.^{9,10} In light of the trends observed for the ESA bands in Eu^{2+} -doped crystals, it now seems reasonable that $\text{Ce}:\text{LiCaAlF}_6$ could offer special advantages over all the other crystals in which Ce had been explored for its laser potential (e.g. LaF_3 , CaF_2 , LiYF_4). In referring back to the data in Fig. 4, it is clearly seen that, in comparison to other hosts, the ESA of $\text{Eu}:\text{LiCaAlF}_6$ is both strongly shifted to shorter wavelengths and much weaker (notice the relative values of the ground state bleaching and the ESA for calibration).

In our studies of the pump-probe spectra of Ce in the LiCaAlF_6 and the related crystal LiSrAlF_6 (known as $\text{Ce}:\text{LiSAF}$), we found an additional nuance concerning the influence of the CB on the states of the RE ion. From the absorption/emission and pump-probe spectra of $\text{Ce}^{3+}:\text{LiSrAlF}_6$ pictured in Figs. 5 and 6 below, the interesting feature is that both the absorption and emission appear to be roughly isotropic, while the pump-induced gain spectrum is indistinctly anisotropic. In fact the n-polarized spectrum offers far more gain than obtained for the a-polarization. This same basic trend was observed for Ce^{3+} in LiCaAlF_6 , although the anisotropy is not as pronounced.

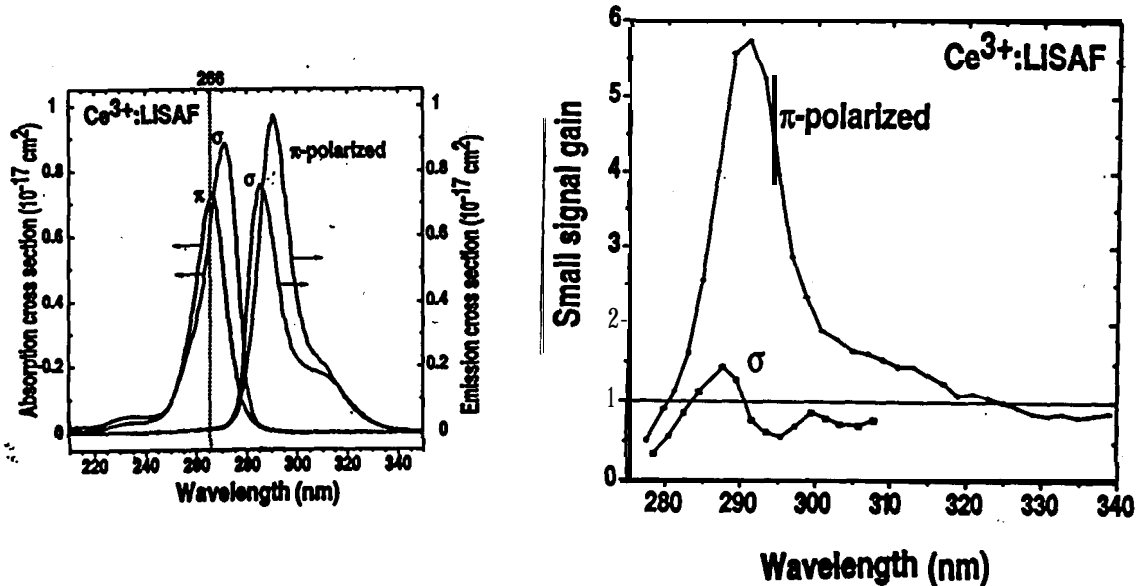


Figure 5: Absorption and emission spectra of Ce^{3+} -doped LiSrAlF_6 . Figure 6: Pump-probe spectra of $\text{Ce}:\text{LiSAF}$.

The anisotropy of the cerium gain spectra can be accounted for by considering the influence of ESA. We are therefore compelled to conclude that the 5d - CB transition is highly anisotropic in this case. By examining the crystal structure plotted below, we notice that the strontium ions occur in layers, suggesting a simple physical mechanism for the hypothesized anisotropy of the CB. First, on the basis of size arguments, we must conclude that the cerium ions substitute for the strontium. Second, if the lowest conduction band states arise from the larger and more polarizable Sr^{2+} ions, and not from the more ionic and smaller Al^{3+} and Li^{+} ions, then the 5d - CB transitions will ostensibly

be a-polarized as the electron transition can be described in principle as an electron movement in the physical direction perpendicular to the c axis.

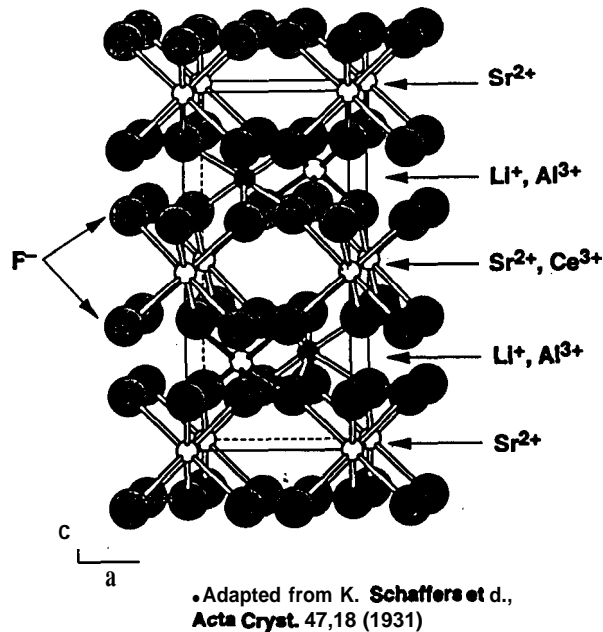


Figure 7: Portrayal of the crystal structure of LiSrAlF_6 .

As the 5d orbitals of the RE ions have been found to exhibit transitions to the CB of the host crystals, it has long been considered that polarization is due to transitions from defects where electrons are trapped to the CB as well. These “color centers” have been observed in the Ce:LiSAF crystals. Figure 8 displays the spectrum observed as a consequence of UV excitation of the crystal. The color center absorption is found to extend into the laser emission region at 290 nm. If we then examine a series of crystals, characterizing both the color center absorption at 290 nm and the laser slope efficiency obtained in a simple confocal cavity with a 266 nm pump source, we find as expected that the two measurements are significantly correlated (see Fig.9).¹¹

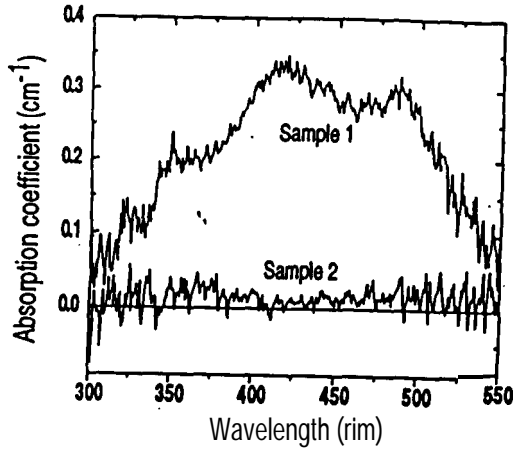


Figure 8: Color center absorption induced in two different Ce:LiSAF by UV light.

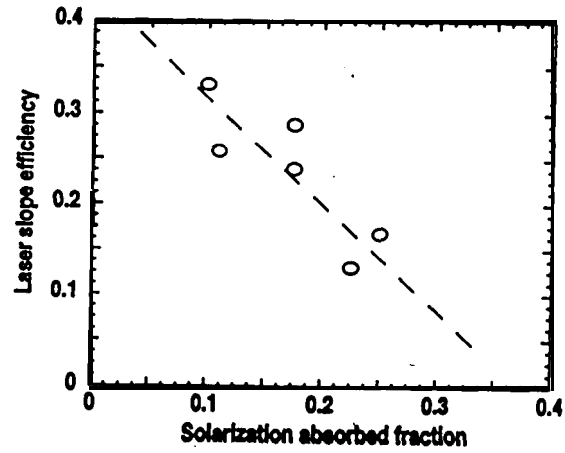


Figure 9: Correlation between the laser slope efficiency and induced color center absorption.

The summary of the processes impacting the Ce:LiSAF laser is portrayed in Fig. 10, including the effects of ESA and polarization. In order to adequately describe the laser, however, one more phenomenon must be included, involving the bleaching of the color centers. This annihilation of the color centers was found to occur at both the 266 nm pump wavelength, as well as at other visible wavelengths that correspond to the color center absorption of Fig. 8. It is interesting to point out that the bleaching effect can be harnessed to increase the efficiency of the laser. In Fig. 11, we show the effect of including the use of a so-called “anti-solarant” pump beam at 532 nm (amounting to the **simultaneous** introduction of the 266 nm fourth harmonic with the second harmonic of a Nd:YAG laser).¹¹ From the data pictured below we can see that the 290 nm output of the Ce:LiSAF laser rises as the **fluence** of the 532 nm beam is increased. On the basis of the absorbed energy of the 266 nm pump, slope efficiencies as high as 47 % have achieved using this approach.

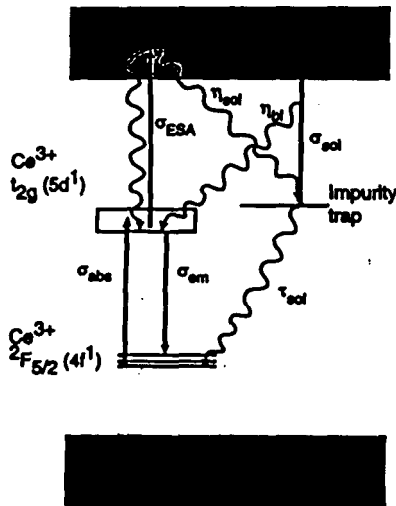


Figure 10: Schematic of the ESA and polarization processes in Ce:LiSAF.

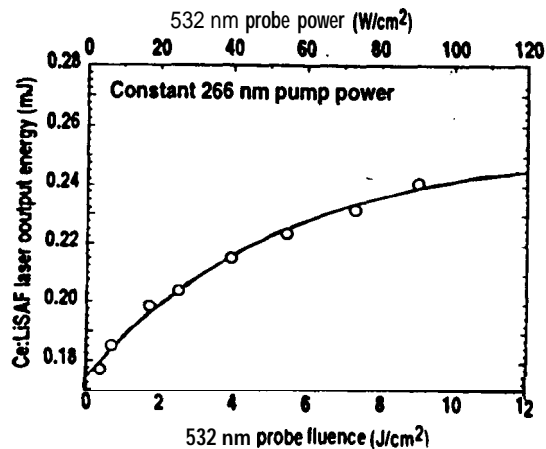


Figure 11: Impact of 532 nm **antisolarant** pump beam on the output of Ce:LiSAF laser oscillator pumped at 266 nm.

5. Summary

We have presented information relating to how the 5d - CB interaction represents one of the crucial **fundamental** issues impacting whether many potential 5d - 4f lasers will or will not prove to be practical and effective devices. We showed that the Sm^{2+} ion happens to be free of interference of the 5d - CB transition because of the placement of bands, while there seems to be a strong tendency for overlap for the Eu^{2+} -doped crystals that we studied, **generally** defeating the prospect for gain in these materials. Studies of the luminescence of Sm in crystals reveals that the mediation of the CB similarly exerts the most important influence over whether the doped material is an efficient emitter or not. One of the surprising results was that $\text{Eu}:\text{LiCaAlF}_6$ had a marked reduction of the strength and overlap of the ESA band and the emission feature. While $\text{Eu}:\text{LiCaAlF}_6$ still does not exhibit gain, the 5d - 4f transition of Ce^{3+} in LiCaAlF_6 and LiSrAlF_6 does indeed offer the best quantified laser performance by a UV solid state laser discovered to date. The laser performance appears to be optimized by also taking advantage of the **anisotropic** character of the CB, such that the laser material is both pumped and **lased** in the π -polarization.

6. References

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